Supporting Information for

Metal-free Aerobic Oxidative Coupling of Amines to Imines

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General Information
D$_2$O and CDCl$_3$ were purchased from Cambridge Isotope Laboratory Inc; water was triply distilled and stored under air; other solvents were also distilled before used; all amines purchased from Aldrich or Alfa Aesar were distilled and stored at 4°C; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. 1H NMR spectra were recorded on a Bruker AVII+400 spectrometer at ambient temperature. GC-MS results were obtained by the Agilent 7890A/5975C GC/MSD system equipped with the DB-17MS (30m, 0.25mm, 0.25um) column. Mass spectra were taken on a Bruker Apex IV FTMS.

General Procedure for the Oxidative Coupling Reactions
In a typical experiment, one atmosphere dioxygen is pressurized to a 45 ml Schlenk flask containing 4-methylbenzylamine (0.073g, 0.6 mmol) and water. After the reaction mixture is refluxed for 48 hours, the product is simply extracted with diethyl ether and characterized by GC, GC-MS and 1H NMR.

For the homo-coupling reactions: 4-Methylbenzyl amine 0.073 g (0.60 mmol) and water 0.60 ml were added into a Schlenk flask with a high vacuum valve (V = 40 ml) fitting in a Radleys parallel synthesis station. The sample was subjected to three freeze-pump-thaw cycles and then filled with 1 atm O$_2$. The solution was stirred vigorously and refluxed for 60 hours. After it was cooled down to room temperature, 2 ml of water was added to the solution. The product was extracted for three times with 9 ml of diethyl ether. The organic layers were combined and diluted to 25.00 ml for GC test.

For the cross-coupling reactions: Benzylamine 0.064 g (0.60 mmol), aniline 0.17 g (1.8 mmol) and water 0.60 ml were used instead.

Temperature of water in this closed system

Temperature of the reactor

Figure 1S. Radleys parallel synthesis station
**Figure 2S.** The kinetics of the formation of N-benzylidene-benzylamine (red) and N-benzylidene-hexamine (black)

**Scheme 1S.** Pathways for the Cross Coupling Reaction

**General Procedure for the Preparations of Imines**

Imines were independently synthesized by condensation of the aldehydes and the amines, and used as standards for GC measurements. The aldehydes and amines were purified by distillation.

For general imines, the procedure is as follows:¹ To a 25 ml round-bottomed flask was added benzylamine (0.8289 g, 7.74 mmol), 5 ml CH₂Cl₂, and 0.5 g MgSO₄. With stirring, benzaldehyde (0.8201 g, 7.73 mmol) was added. The mixture was stirred at room temperature for 3 hours and then filtered to remove MgSO₄ solid. The filtrated solution was collected and the solvent was removed by rotary evaporation giving a colorless liquid. The excess aldehydes and amines were further removed under high vacuum (< 0.1 Pa) at 60 °C. The yield was 95%.

For the synthesis of N-(diphenylmethylene)-diphenylmethamine, the procedure is as follows:² Benzophenone 2.73 g (15 mmol) and diphenylmethamine 3.02 g (16.5 mmol) were combined and treated with one drop of concentrated H₂SO₄. The Si(OEt)₄ 3.45 g (16.5 mmol) was added and the mixture placed in a flask equipped with a still head. The solution was heated at 160 °C under nitrogen overnight. The distillate (EtOH) was discarded and the residue was dissolved in Et₂O (50 ml) and washed with saturated NaHCO₃ solution and H₂O (25 ml each). The Et₂O solution was dried (MgSO₄) and the solvent was removed under vacuum. Crude products were purified by kugelrohr distillation. For further purification the imine (2 g) was dissolved in 10 ml of 95% EtOH and treated with 2 ml of 1 M KOH in EtOH. The solution was stirred for 15 minutes than filtered and the precipitated washed with Et₂O. The filtrate was washed with H₂O (2 × 20 ml) and dried (MgSO₄). The solvent was removed under vacuum to yield the purified imine.
General Procedure for the Aza-D-A Reactions

After the oxidative coupling reaction, the product was extracted with diethyl ether. The solvent was removed under vacuum. To the residue was added 2 ml of methanol. Under stirring at room temperature, Danishefsky’s diene 58 $\mu$L (0.30 mmol) was added dropwise in 10 minutes to the reaction mixture. After stirring for 1 hour at room temperature, another 58 $\mu$L of Danishefsky’s diene was added dropwise in 10 minutes. The reaction mixture was stirred for another 1 hour at room temperature and quenched with 2 ml of 1.0 M HCl. The product was extracted with diethyl ether and concentrated. The crude material was purified by column chromatography with CH$_2$Cl$_2$/EA (4:1 V/V) as eluent.

Spectral Data for Products

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 4.80 (s, 2H), 7.19-7.32 (m, 1H), 7.32-7.33 (m, 4H), 7.37-7.41 (m, 3H), 7.76-7.78 (m, 2H), 8.36 (s, 1H).

$^1$C NMR (CDCl$_3$, 100MHz): $\delta$ 65.12, 127.06, 128.06, 128.36, 128.57, 128.67, 130.82, 136.30, 139.43, 162.00.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 2.32 (s, 3H), 2.36 (s, 3H), 4.75 (s, 2H), 7.13 (d, 2H), 7.20-7.22 (m, 4H), 7.65 (d, 2H), 8.32 (s, 1H).

$^1$C NMR (CDCl$_3$, 100MHz): $\delta$ 21.20, 21.59, 64.90, 128.06, 128.35, 129.25, 129.39, 133.80, 136.52, 136.58, 141.03, 161.73.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 4.74 (s, 2H), 7.24 (d, 2H), 7.28-7.31 (m, 2H), 7.35-7.38 (m, 2H), 7.67-7.70 (m, 2H), 8.30 (s, 1H).

$^1$C NMR (CDCl$_3$, 100MHz): $\delta$ 64.23, 128.72, 129.01, 129.35, 129.55, 132.90, 134.58, 136.95, 137.74, 160.88.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 4.75 (s, 2H), 6.99-7.04 (m, 2H), 7.06-7.10 (m, 2H), 7.26-7.30 (m, 2H), 7.74-7.77 (m, 2H), 8.32 (s, 1H).

$^1$C NMR (CDCl$_3$, 100MHz): $\delta$ 64.22, 115.30, 115.51, 115.72, 115.93, 129.54, 129.61, 130.23, 130.32, 132.45, 132.48, 135.07, 135.10, 160.62, 160.88, 163.26, 163.31, 165.76.
$^1$H NMR (CDCl$_3$, 400MHz): δ 3.77 (s, 3H), 3.81 (s, 3H), 4.71 (s, 2H), 6.86-6.92 (m, 4H), 7.23 (d, 2H), 7.70 (q, 2H), 8.28 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): δ 55.33, 55.41, 64.46, 113.99, 114.06, 129.24, 129.30, 129.89, 131.78, 158.74, 160.99, 161.76.

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$^1$H NMR (CDCl$_3$, 400MHz): δ 2.38 (s, 3H), 2.49 (s, 3H), 4.81 (s, 2H), 7.14-7.30 (m, 7H), 7.90-7.92 (m, 1H), 8.65 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): δ 19.37, 19.48, 63.38, 126.17, 126.27, 127.15, 127.84, 128.41, 130.21, 130.33, 130.91, 134.35, 136.20, 137.71, 137.82, 160.64.

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$^1$H NMR (CDCl$_3$, 400MHz): δ 5.40 (s, 2H), 7.44-7.58 (m, 7H), 7.79-7.93 (m, 5H), 8.24 (d, 1H), 8.93 (d, 1H), 9.07 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): δ 63.39, 124.11, 124.61, 125.36, 125.77, 125.84, 126.04, 126.17, 126.27, 127.34, 127.96, 128.75, 128.84, 129.30, 131.27, 131.82, 131.86, 133.98, 134.03, 135.67, 162.09.

FTMS (ESI): m/z calcd for C$_{22}$H$_{18}$N$^+$ ([M + H]$^+$): 296.14338; found: 296.14330.

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$^1$H NMR (CDCl$_3$, 400MHz): δ 4.92 (s, 2H), 6.95-6.98 (m, 2H), 7.03-7.05 (m, 1H), 7.20-7.22 (m, 1H), 7.29-7.30 (m, 1H), 7.38-7.39 (m, 1H), 8.38 (d, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): δ 58.58, 124.88, 125.34, 126.95, 127.45, 129.39, 131.02, 141.65, 142.23, 155.46.

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$^1$H NMR (CDCl$_3$, 400MHz): δ 5.55 (s, 1H), 7.06-7.08 (m, 2H), 7.16-7.20 (m, 2H), 7.24-7.28 (m, 4H), 7.31-7.37 (m, 7H), 7.39-7.43 (m, 3H), 7.74-7.76 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 100MHz): δ 70.02, 126.81, 127.72, 127.90, 128.14, 128.47, 128.54, 128.61, 128.90, 130.19, 136.87, 139.99, 145.03, 167.04.

FTMS (ESI): m/z calcd for C$_{26}$H$_{22}$N$^+$ ([M + H]$^+$): 348.17468; found: 348.17442.

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$^1$H NMR (CDCl$_3$, 400MHz): δ 7.20-7.22 (m, 3H), 7.36-7.40 (m, 2H), 7.44-7.47 (m, 3H), 7.88-7.92

$^1$H NMR (CDCl$_3$, 400MHz): δ 7.20-7.22 (m, 3H), 7.36-7.40 (m, 2H), 7.44-7.47 (m, 3H), 7.88-7.92
(m, 2H), 8.44 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 120.99, 126.05, 128.89, 128.93, 129.27, 131.48, 136.37, 152.23, 160.49.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 2.36 (s, 3H), 7.13 (d, 2H), 7.18 (d, 2H), 7.44-7.47 (m, 3H), 7.87-7.90 (m, 2H), 8.45 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 21.13, 120.94, 128.83, 128.85, 129.88, 131.31, 135.91, 136.50, 149.60, 159.68.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 7.12-7.15 (m, 2H), 7.32-7.35 (m, 2H), 7.45-7.49 (m, 3H), 7.87-7.89 (m, 2H), 8.41 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 122.33, 129.00, 129.35, 131.58, 131.73, 136.09, 150.64, 160.80.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 0.88 (t, 3H), 1.28-1.35 (m, 8H), 1.66-1.73 (m, 2H), 3.58-3.62 (m, 2H), 7.36-7.41 (m, 3H), 7.70-7.74 (m, 2H), 8.26 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 14.20, 22.76, 27.46, 29.26, 31.07, 31.95, 61.94, 128.14, 128.68, 130.53, 136.55, 160.79.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 0.89 (t, 3H), 1.29-1.38 (m, 6H), 1.66-1.73 (m, 2H), 3.58-3.62 (m, 2H), 7.39-7.40 (m, 3H), 7.70-7.73 (m, 2H), 8.26 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 14.19, 22.74, 27.16, 31.02, 31.80, 61.94, 128.13, 128.67, 130.53, 136.52, 160.79.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 2.68 (dd, 1H), 2.84 (dd, 1H), 4.12 (d, 1H), 4.34 (d, 1H), 4.50 (t, 1H), 5.08 (d, 1H), 7.12 (d, 2H), 7.24-7.25 (m, 2H), 7.28-7.36 (m, 7H).

$^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 43.80, 57.35, 60.80, 98.84, 127.19, 127.83, 128.31, 128.42, 129.02,
129.13, 136.00, 138.69, 154.26, 190.40.

FTMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{18}\text{NO}^+$ ([M + H]$^+$): 264.13829; found: 264.13800.

![Chemical structure 1]

$^1\text{H NMR}$ (CDCl$_3$, 400MHz): $\delta$ 2.63 (dd, 1H), 2.80 (dd, 1H), 4.07 (d, 1H), 4.32 (d, 1H), 4.32 (t, 1H), 5.10 (d, 1H), 7.05 (d, 2H), 7.17 (d, 2H), 7.27 (d, 1H), 7.31-7.34 (m, 4H).

$^{13}\text{C NMR}$ (CDCl$_3$, 100MHz): $\delta$ 43.74, 56.73, 60.22, 99.54, 128.57, 129.15, 129.30, 129.42, 134.25, 134.39, 137.03, 153.95, 190.02.

FTMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{NO}^+$ ([M + H]$^+$): 332.06035; found: 332.06008.

![Chemical structure 2]

$^1\text{H NMR}$ (CDCl$_3$, 400MHz): $\delta$ 2.34 (s, 6H), 2.64 (dd, 1H), 2.77 (dd, 1H), 4.06 (d, 1H), 4.27 (d, 1H), 4.44 (t, 1H), 5.05 (d, 1H), 7.01 (d, 2H), 7.14 (m, 6H), 7.26 (d, 1H).

$^{13}\text{C NMR}$ (CDCl$_3$, 100MHz): $\delta$ 21.15, 43.81, 56.88, 60.40, 98.48, 127.08, 127.82, 129.59, 129.69, 132.88, 135.72, 137.99, 138.07, 154.17, 190.50.

FTMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}^+$ ([M + H]$^+$): 292.16959; found: 292.16927.

Reference


Spectra of Products

Figure 3S. The $^1$H NMR of N-benzylidenebenzylamine
**Figure 4S.** The $^{13}$C NMR of N-benzylidenebenzylamine

![N-benzylidenebenzylamine](image)

**Figure 5S.** The $^1$H NMR of N-(4-methylbenzylidene)-p-methylbenzylamine

![N-(4-methylbenzylidene)-p-methylbenzylamine](image)

**Figure 6S.** The $^{13}$C NMR of N-(4-methylbenzylidene)-p-methylbenzylamine

![N-(4-methylbenzylidene)-p-methylbenzylamine](image)
Figure 7S. The $^1$H NMR of N-(4-chlorobenzylidene)-p-chlorobenzylamine

Figure 8S. The $^{13}$C NMR of N-(4-chlorobenzylidene)-p-chlorobenzylamine
Figure 9S. The $^1$H NMR of N-(4-fluorobenzylidene)-p-fluorobenzylamine

Figure 10S. The $^{13}$C NMR of N-(4-fluorobenzylidene)-p-fluorobenzylamine
Figure 11S. The $^1$H NMR of N-(4-methoxybenzylidene)-p-methoxybenzylamine

Figure 12S. The $^{13}$C NMR of N-(4-methoxybenzylidene)-p-methoxybenzylamine
Figure 13S. The $^1$H NMR of N-(2-methylbenzylidene)-o-methylbenzylamine

Figure 14S. The $^{13}$C NMR of N-(2-methylbenzylidene)-o-methylbenzylamine
Figure 15S. The $^1$H NMR of 1-(naphthalen-1-yl)-N-(naphthalen-1-ylmethylene)methanamine

Figure 16S. The $^{13}$C NMR of 1-(naphthalen-1-yl)-N-(naphthalen-1-ylmethylene)methanamine
Figure 17S. The $^1$H NMR of thiophen-2-yl-N-(thiophen-2-ylmethylene)methanamine

Figure 18S. The $^{13}$C NMR of thiophen-2-yl-N-(thiophen-2-ylmethylene)methanamine
Figure 19S. The $^1$H NMR of N-diphenylmethylenediphenylmethylamine

Figure 20S. The $^{13}$C NMR of N-diphenylmethylenediphenylmethylamine
Figure 21S. The $^1$H NMR of N-benzylideneaniline

Figure 22S. The $^{13}$C NMR of N-benzylideneaniline
**Figure 23S.** The $^1$H NMR of N-benzylidene-4-methylaniline

**Figure 24S.** The $^{13}$C NMR of N-benzylidene-4-methylaniline
Figure 25S. The $^1$H NMR of N-benzylidene-4-chloroaniline

Figure 26S. The $^{13}$C NMR of N-benzylidene-4-chloroaniline
**Figure 27S.** The $^1$H NMR of N-benzylideneheptanamine

**Figure 28S.** The $^{13}$C NMR of N-benzylideneheptanamine
Figure 29S. The $^1$H NMR of N-benzylidenehexanamine

Figure 30S. The $^{13}$C NMR of N-benzylidenehexanamine
Figure 31S. The $^1$H NMR of 1-benzyl-2-phenyl-2,3-dihydropyridin-4(1H)-one

Figure 31S. The $^{13}$C NMR of 1-benzyl-2-phenyl-2,3-dihydropyridin-4(1H)-one
Figure 33S. The $^1$H NMR of 1-(4-chlorobenzyl)-2-(4-chlorophenyl)-2,3-dihydropyridin-4(1H)-one

Figure 34S. The $^{13}$C NMR of 1-(4-chlorobenzyl)-2-(4-chlorophenyl)-2,3-dihydropyridin-4(1H)-one
Figure 35S. The $^1$H NMR of 1-(4-methylbenzyl)-2-p-tolyl-2,3-dihydropyridin-4(1H)-one

Figure 36S. The $^{13}$C NMR of 1-(4-methylbenzyl)-2-p-tolyl-2,3-dihydropyridin-4(1H)-one